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Electronic and Atomic Structure of Semiconductors  
and of High-Temperature Superconductors

Final Technical Report

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by

E. Tosatti and R. Car

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## SUMMARY

In this final technical report we summarize the activity carried out within the present research project, conducted over a three year period, under the sponsorship of the European Research Office of the U.S. Army. The work done covers different areas, namely :

- Microscopic simulations of solid, amorphous and liquid semiconductors and semimetals, of their defects, vacancies, and surfaces, and of hydrogen diffusion , using Car-Parrinello and related methods;
- Theory of the electronic and vibrational properties of semiconductors, semiconductor alloys, interfaces, microstructures, and of GaAs - based semiconductor superlattices;
- Quantum simulations and theory of highly correlated electron systems , particularly as models for high- $T_c$  superconducting materials;

The body of the report will briefly outline the work done in each area, and highlight the main achievements which have been made possible by the project.

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## LIST OF KEYWORDS

- simulation, ab initio molecular dynamics , amorphous semiconductors, semimetals, vacancies in semiconductors, semiconductor surfaces, hydrogen diffusion , Car-Parrinello methods, semiconductor electronic structure, semiconductor vibrational properties, semiconductor alloys, semiconductor interfaces, band offset, GaAs , semiconductor superlattices, large-scale algorithms, quantum simulations, quantum Monte Carlo, Lanczos diagonalization, highly correlated electrons , Hubbard model , t-J model, non-Fermi liquid, quantum Hall effect, high- $T_c$  superconductivity;

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## SECTION 1

**Microscopic simulations of solid, amorphous and liquid semiconductors and semimetals, of their defects, vacancies, and surfaces, and of hydrogen diffusion, using Car-Parrinello and related ab initio (molecular dynamics plus local density electronic structure) methods.**

The SISSA condensed matter theory group in Trieste has developed, during the 80's, very innovative computational methods, which match together the quantum-mechanical accuracy of first-principles electronic structure calculations (local density Kohn-Sham approach), and the direct, realistic classical simulation of ion motion characteristic of classical molecular dynamics.

One of the main goals of the present project has been to apply these novel methods to simulate the behavior, and to uncover the properties of systems of high current interest, both physical and technological. Highest priority has been given to semiconductors and semimetals (Si, Ge, diamond, Ga, GaAs), solid as well as liquid.

### 1.1 Ab initio simulation of melted semiconductors

The melting transition of silicon and other physically and technologically important semiconducting elements and compounds is peculiar. The liquid, unlike the solid, is a metal. Moreover, these systems contract at melting, instead of expanding. Prior to the development of ab-initio molecular dynamics, it had not been possible to understand this phenomenology at a quantitative microscopic level.

(i) An accurate first-principle simulation of liquid silicon (l-Si) has allowed an (unprecedented) computation of structural, dynamical and electronic properties of this very special liquid [1-3]. Perhaps the most notable result of this investigation has been the identification, in the metallic liquid, of covalent tetrahedral fluctuations which play an important role in many of the properties of l-Si.

(ii) Amorphous and liquid GaAs systems have been simulated [2-5] using a technique similar to that used for l-Si. This has been the first ab-initio

simulation of a compound liquid system. Structural, dynamical and electronic properties have been calculated. Of particular interest is the calculation of partial pair correlation functions, which are not yet known

from experiment. These studies indicate that, even in the metallic liquid, and similar to l-Si, the bonding in GaAs does retain strongly covalent remnant characters.

1.2 Defects in semiconductors: simulation of hydrogen diffusion and vacancy diffusion in silicon, and of properties of impurities in diamond.

Impurities are crucial in determining the properties of semiconductors. In order to understand impurities in semiconductors, an accurate determination of a) static geometrical parameters (where does exactly the impurity go in space? how does it distort the lattice around itself?), of b) the electronic structure, as well as of c) the dynamics (impurity vibrations, impurity diffusion mechanism and rate), are basic. Most elusive and important, are hydrogen and vacancies in silicon.

(i) A fully dynamical Car-Parrinello simulation of high temperature diffusion of H in crystalline silicon (c-Si) has been carried out within this project [6-8]. The calculated diffusion coefficient is in excellent agreement with experiments in the same temperature range. Important dynamical effects occurring at high temperature have been identified. This has already become a very well-known piece of work, in the semiconductor literature.

(ii) Vacancy induced self-diffusion in silicon at high temperature has been studied with ab-initio molecular dynamics techniques. This study has led to identification of a number of processes, like vacancy double jumps and temporary formation of extended vacancies at high temperature, which significantly enhance self-diffusion and are responsible for known non-Arrhenius behaviour of the self-diffusion coefficient [9,10].

(iii) Diamond, though obviously not a regular semiconductor, is becoming increasingly important. Using the Car-Parrinello method, n-type dopants in diamond have been studied, in collaboration with an american group [11].

### 1.3 Simulation of amorphous silicon, pure and hydrogenated

Doped amorphous silicon is an important material, particularly for energy and device applications. Passivation of dangling bonds by hydrogen has been shown in the 70's to be the crucial step that allows doping.

Within the present project, a realistic hydrogenated amorphous silicon (a-Si:H) configuration has been generated by simulated quenching from the melt in a Car-Parrinello-generated 1-Si sample with about 11% H concentration, typical of device quality material. The structural and vibrational properties of the simulated system were in excellent agreement with several experimental data. Hydrogen was confirmed to passivate Si dangling bonds. It also showed a tendency to be inhomogeneously distributed throughout the sample with some clustering effects. [7,8,12,13].

### 1.4 A covalent semimetal: gallium

Gallium is noteworthy, for several reasons. In physics, it is perhaps the one element where competition between covalency and metallicity is the strongest. In technology, it enters GaAs as a constituent. Ga films on the semiconductor are very often used as prototype metal-semiconductor contact.

(i) New results on structure and bonding of solid Gallium have been obtained, using ab-initio techniques similar to those used for Si and GaAs. The competition between covalency and metallicity, which is embodied in the stable crystalline form (alpha-gallium), is shown to account for many of the strange properties of this semimetal. The remarkable conclusion which emerges from this study is that Ga is the only element whose stable zero-pressure crystalline form consists of diatomic molecules ( $\text{Ga}_2$ ), with sufficient overlap to give a metal, instead of an insulator, as for instance in solid  $\text{H}_2$ . [14].



(ii) First-principles calculations of the properties of liquid gallium have also been carried out. They demonstrate the presence, even at temperatures as high as three times the melting temperature, of fluctuating binary bonds, remnants of those present in solid  $\alpha$ -Ga. We have found that a two-fluid modeling (atomic fluid, coexisting with molecular fluid) helps representing situations of this kind very effectively [15].

### 1.5 Semiconductor and semimetal surfaces

Clean, controlled surfaces are very basic in the study of semiconductors, and related systems and problems. After developing the new ab-initio simulation methods, the long-standing interest of our group in surface properties has found the natural computational means for progress. During the tenure of this project, we have carried out the very first large-scale surface simulations for semiconductors and semimetals, a very demanding, but very rewarding, calculational effort.

(i) We have started, most naturally, with simulations of Silicon surfaces. Clean Si(111) has been studied first. The ideal surface has been shown to be unstable even at very low temperatures, and to undergo a remarkable and extremely fast conversion to a (2x1) reconstructed form [16]. This exhibits precisely the surface "pi-bonded chains" predicted long ago by Pandey, and confirmed by several experimental facts. Dynamical properties, like surface phonons, can also be extracted from these studies [16]. We have then made a study of vacancies on Si(111)2x1 [17,18], and of hydrogen on Si(100) [19,20], both of which are useful in identifying the role of surface defects. A new vacancy-assisted reconstruction of Si(111) has been discovered [21]. Moreover, hydrogen-induced deconstruction from Si(111)2x1 to Si(111)1x1/H has been demonstrated [22].

(ii) Semiconductor surface simulation work has been continued and extended to germanium surfaces. The reconstructed ground state of Ge(111)2x1 has been studied, and found to be also of the pi-bonded chains type [23,24] but with a much larger "surface buckling" than on Si(111). Next, we have considered the stable adatom-stabilized reconstruction of Ge(111), which has a 2x8 surface periodicity. We have analysed this Ge(111)2x8 surface in great depth, a study which has led so far to several

pieces of work, one on the exact prediction of the complicated zero-temperature structure [25-27], and two more in advanced progress, on the high-temperature properties and phase transitions of this important surface [28].

(iii) Semimetal surface work is basically non-existent so far. Having stimulated recent STM experiments on Gallium surfaces, we have undertaken a parallel series of simulations directed at establishing in detail the unknown structure and properties of Ga(001) and Ga(010). While the latter turns out to look relatively close to ideal, results have been much more exciting for Ga(001). In the stable state, we predict this surface of alpha-gallium to be "coated" with two surface layers of a different gallium crystalline phase, the so-called Ga III (dense metallic) phase [29]. This surprising prediction, while accounting in a very natural manner for the existing STM data, will now be tested by newer, more stringent experiments.

(iv) Diamond surfaces are receiving increasing attention, due also to recent attempts at growing diamond coatings for efficient protection and heat dissipation of underlying semiconductor devices. Diamond is a difficult system, both experimentally and theoretically. In order to deal with the (111) diamond surface, we were forced to deploy a very considerable human and computational effort, which lasted just over a year. The outcomes, however, seem well worthwhile. We find this surface to undergo spontaneous  $2 \times 1$  reconstruction with the same pi-bonded chains amount of Si and Ge(111). Unlike these surfaces, however, there is no chain buckling. We predict instead a remarkable chain dimerization, by an amount which makes the pi-bonded chain of this clean diamond surface very similar to a polyacetylene chain, known to be also pi-bond dimerized, and by about the same amount! Moreover, we find the calculated dimerization to decrease gently with temperature, until an instability is reached at about 2600 K. Here, we speculate that the diamond surface might undergo "graphitization" [30].

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## Section 2

## Theory of the electronic and vibrational properties of semiconductors, semiconductor alloys, interfaces, microstructures, and GaAs-based semiconductor superlattices

The research carried out under this section has proceeded along four main lines. 1) Vibrational properties of semiconductor pure crystals, alloys, and superlattices. 2) Theory of the band offsets at semiconductor heterojunctions. 3) Theory of the structure and phase stability of semiconductor alloys. 4) Development of new algorithms for the calculation of the electronic structure of extended systems.

**1. Vibrational properties.** A major breakthrough in the *ab-initio* calculation of the vibrational properties of extended systems has been opened by the introduction of the so called Baroni-Giannozzi-Testa approach to density-functional perturbation theory.<sup>a</sup> This approach has been successfully applied to the calculation of the piezoelectric properties of pure semiconductor crystals,<sup>5,29</sup> their phonon dispersions<sup>9,27,28</sup> the vibrational modes of perfect, short-period GaAs/AlAs superlattices,<sup>1</sup> and of Si surfaces.<sup>11</sup> The ease by which the dynamical matrices of semiconductors can be obtained at arbitrary wavevectors has opened the possibility of calculating accurate *real-space* interatomic force constants.<sup>9,28</sup> The force constants so calculated have found wide application in the calculation of the vibrational properties of complex semiconductor systems, such as alloys,<sup>4,7,25,28</sup> and (possibly disordered) superlattices.<sup>8,14,16,19,20</sup> In the case of GaAs/AlAs superlattices, our main result has been to reveal how Raman spectroscopy of AlAs-like optical modes can be used as a very sensitive probe for the quality characterization of the interfaces. Our theoretical research in this field has lead us to a close collaboration with leading experimental groups.<sup>16</sup> These techniques have been also applied to the study of the low-symmetry phases occurring in Cesium halides at megabar pressures.<sup>23</sup>

**2. Band offsets.** We have developed a general quantum mechanical theory of band offsets at semiconductor heterojunctions,<sup>b</sup> which we have systematically applied to a wide variety of technologically relevant cases, including common-ion<sup>b</sup> as well as no-common-ion,<sup>2</sup> lattice-matched<sup>b,2</sup> as well as mismatched,<sup>3,15,26</sup> isovalent,<sup>b,3,15</sup> as well as heterovalent<sup>b,24</sup> heterostructures. Our theory has lead to *predict* the possibility of tuning the band offsets at isovalent interfaces, by doping them by an ultrathin layer of an heterovalent semiconductor.<sup>b,10</sup> This theoretical prediction has been confirmed by several experimental investigations, and it has lead us to a close collaboration with leading experimental groups.<sup>18,21,24</sup>

**3. Structure of alloys.** We have developed a new computational scheme to deal with the structural and thermodynamical properties of semiconductor alloys.<sup>6,12,22</sup> In our scheme, each disordered configuration of the alloy is treated as a perturbation with respect to an

<sup>a</sup> S. Baroni, P. Giannozzi, and A. Testa, Phys. Rev. Lett. **58**, 1861 (1987).

<sup>b</sup> S. Baroni, R. Resta, A. Baldereschi, and M. Peressi, in *Spectroscopy of Semiconductor Microstructures*, edited by G. Fasol, A. Fasolino, and P. Lugli, NATO ASI Ser. B, no 206 (Plenum, New York, 1989), p. 251.

appropriate periodic system (the *virtual crystal*), which is treated by density-functional perturbation theory.<sup>a</sup> It can be shown that, up to second order in the strength of the perturbation, the system can be *exactly* mapped onto a lattice gas with long-range two-body interactions, where the interaction constants are particular linear-response functions of the virtual crystal. Once these response functions have been calculated once for all, the energy of each configuration can be calculated very inexpensively by means of the auxiliary lattice-gas, opening thus the way to large-scale Monte Carlo simulations.

**4. New algorithms.** Two major challenges in the computational materials science of the next decade are the calculation of the electronic structure of very large systems (several hundreds or, possibly, thousands atoms), and the accurate account of the electronic correlations in *real materials* (as opposed to *models*). The computational study of very large systems is presently hindered by the so called  $N^3$  *bottleneck*: the computational workload required by current algorithms scales as the cube of the system size. We have developed a new algorithm whose computational complexity is only linear in the system size,<sup>17</sup> and we are presently applying it to the study of some Germanium microstructures. As for electronic correlations, we have succeeded in applying the *Auxiliary-Field Monte Carlo* technique (previously successfully applied only to lattice models) to realistic hamiltonians for small molecules.<sup>30</sup>

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## SECTION 3

**Quantum simulations and theory of highly correlated electron systems , and models for high- $T_c$  superconducting materials.**

The discovery by von Klitzing of the Quantum Hall Effect in 1980, by Tsui and Stoermer of the Fractional Quantum Hall Effect in 1983, by Mueller and Bednorz of high- $T_c$  superconductivity in 1986, and by Haddon and Hebard of superconductivity in the fullerenes in 1991, have not only marked a new era in their respective fields. They have also shaken to the foundations the existing (and painfully built) home of our theoretical understanding , namely conventional many-body theory.

The main reason for this can be traced to the extremely non-perturbative nature of the new problems, in contrast with the generally perturbation-based substance of the old ones. For instance, in the fractional Hall effect, electron scatter each other but *cannot* exit a given Landau level. In the  $t$ - $J$  , or large  $U$  Hubbard, modeling of a cuprate electronic structure, electrons are not interacting , but then again they *cannot* overlap on the same site. And so on.

The labour of re-building a new home to the many-body theory, one which should encompass the new with the old, is often called, improperly, the theory of strongly correlated systems. In reality , such a theory does not exist yet; for the work has begun, but is only halfway through.

That part of our group which is engaged in the present project , although moved originally by more down-to-earth motivations related with the real materials, has found itself anyway contributing to this effort. We have done this largely , although not uniquely, relying on our tradition in computational physics. This has led for example to new powerful home-made algorithms for fermion Quantum Monte Carlo, and for large-scale diagonalization. Among a variety of strongly correlated toy problems, the Hubbard model is the one we have tried more consistently, we believe with well-recognized results.

4

### 3.1 One -dimensional Hubbard model

The Hubbard model simply consists of electrons moving on a lattice, interacting through an on-site repulsion  $U$ . The prototype of a strongly correlated system, it is a hard, vicious problem: not at all innocent as it may seem. In 1D, it was solved exactly in 1968 by Lieb and Wu; in 2D or higher dimensions, nobody knows how to solve it. Even in 1D, there are many relevant things the exact solution does not give us. Most importantly, the asymptotic behavior of correlation functions. Understanding the 1D case totally, is an important step in the art of learning how to decipher the behavior of strongly correlated systems.

(i) Using newly devised techniques of exact diagonalization, coupled with finite-size scaling of correlation functions, we have calculated the non-Fermi liquid exponents of the one-dimensional Hubbard model [1];

(ii) We have applied the Fermi Hyper Netted Chains (FHNC) Correlated Basis Functions (CBF) method, never implemented on a lattice model so far, to the 1D Hubbard model, with instructive results for the paramagnetic state [2,3]. The effects of strong correlations on the antiferromagnetic Spin Density Wave state has subsequently been studied with the FHNC CBF method[4].

(iii) New techniques and methods have been devised, which are applicable to strongly correlated systems, with the FHNC CBF approach. One has been to use the so-called shadow wave functions[5]. Another, more recent, has been to derive a dramatically simplified FHNC expansion, named Gutzwiller Hyper Netted Chains (GHNC), for Gutzwiller-type wave functions [6]

(iv) Using the Ogata-Shiba factorization of the infinite  $U$ , one dimensional Lieb-Wu wave function, it has proven possible to calculate exactly a dynamical property, in particular the electron Green's function, which had been essentially unknown so far [7].

### 3.2 Two, three, and infinite-dimensional Hubbard model

More realistically, in 2D, 3D, and even in infinite D, one wants to

understand the phase diagram of the Hubbard model as a function of electron filling, and in particular whether to expect a Fermi Liquid or not. This is eventually of importance for the real materials, where it is believed that non-Fermi liquid behavior may be at the origin of novel superconductivity mechanisms.

(i) We have carried out a numerical study of the 2D Hubbard model by quantum Monte Carlo plus finite-size scaling at half filling. This study definitively demonstrates the presence of long-range antiferromagnetic order for the half-filled square lattice [8].

(ii) Using a new powerful diagonalization technique, alternative but equivalent to the Lanczos method, we have studied the 2D Hubbard model on a  $4 \times 4$  square lattice, for arbitrary  $U$ . The results are extremely informative because of their exact nature [9-11].

(iii) Quantum Monte Carlo simulations have been made for a single hole in the 2D Hubbard model at half filling. By calculating in particular the wavefunction renormalization factor  $Z$ , one obtains indications about the possible non-Fermi liquid behavior in 2D [12, 13].

(iv) A quantum Monte Carlo study of the correlation behavior of two holes in the 2D Hubbard model clearly demonstrates the lack of hole-hole attraction, and of hole-hole binding, in the two-dimensional repulsive Hubbard model [14].

(v) An exact non-perturbative solution of the  $D=2$  Hubbard model has been obtained for any finite number of electrons, in the zero-density limit [15, 16]. No direct evidence for non-Fermi liquid has been found in this limit. These results are now widely quoted and used as an important check for other approximate theories.

(vi) Two 1D Hubbard chains coupled by interchain hopping are a useful system for studying the crossover from 1D to 2D behavior. We have carried out a series of studies, based on a combination of renormalization

group approaches, bosonization approaches, and exact diagonalizations, which has been very fruitful. A rich phase diagram is obtained, with strong-coupling phases replacing the 1D Luttinger liquid even for very weak interchain hopping. The relative importance of anomalous Fermi surface exponents versus charge-spin separation have been assessed [17-20].

(vii) A novel semimetal- antiferromagnetic insulator quantum phase transition has been discovered for the 2D Hubbard model on the honeycomb lattice, using quantum Monte Carlo [21].

(viii) The infinite-dimensional Hubbard model has been solved, by the usual method of transforming it to an effective impurity problem, on the hyper-diamond lattice, which is semimetallic at  $U=0$ . We have studied both the semimetal-antiferromagnetic insulator transition already seen in 2D [21], and one between metastable semimetal- paramagnetic insulator, which is a prototype Mott transition [22];

### 3.3 Heisenberg and t-J models

In the large  $U$  limit, the Hubbard model tends to the Heisenberg model at half filling, and more generally to the t-J model at arbitrary filling. Special techniques must be implemented in this limit, where interactions project double occupied configurations out of the ground state.

(i) We have speculated on the possible relativistic spinor character of excitations in the nearly half-filled Hubbard model, and on related consequences for doped antiferromagnets in  $D=3$  space dimensions [23];

(ii) Exact implementation of the single-occupancy constraint, often violated by approximate theories, has been shown to bring about interesting modifications to the physics of flux, dimer, and chiral metastable phases of the large- $U$  2D Hubbard model at half filling [24-26].

(iii) A new consistent spin-wave theory has been constructed for finite lattices. As a test case, we have considered the 2D second-neighbor (so-called  $J_1 - J_2$ ) Heisenberg model, with excellent results [27];

(iv) Systematically constructed variational wavefunctions have been used to study the lightly doped, large-spin t-J model, with particular emphasis on phase separation phenomena at large  $J$  [28];

### 3.4 Fullerenes

During the tenure period of this project, superconductivity in alkali-doped fullerenes at relatively high temperature was discovered experimentally by an american group. In Trieste, we started a fresh research line on the new fullerene superconductors, with emphasis on the possible role of strong correlation phenomena.

(i) Based on the known observation that paramagnetic behavior prevails in partly occupied degenerate molecular orbitals of large organic molecules, we speculate on the role of virtual triplet-singlet excitations in fullerene, and on a possible ensuing negative effective Hubbard  $U$  [29].

### 3.5 Possible macroscopic coherence in quantum paraelectrics

We have started new work on possibly exciting properties of a totally different strongly correlated system, the quantum paraelectric  $\text{SrTiO}_3$ .

(i) A new, non-structural, phase transition has been discovered at 37 K in  $\text{SrTiO}_3$ , and given a tentative discussion in a joint experimental-theoretical paper with K. A. Mueller (discoverer of high- $T_c$  superconductivity) [30].

(ii) Model hamiltonians appropriate for quantum paraelectrics, and a first study of their phase diagrams have been considered in a displacive context [31], and more recently in a lattice model [32]. This work is still in a development stage.

### 3.6 Fractional quantum Hall effect

The quantum Hall effect is an outstanding phenomenon, for its importance and beauty. While there is a solid understanding of quantisation for odd denominators, phenomena at even denominator fillings are subtler, and much less understood.

(i) We have continued very early work on the state at half filling, based on a numerical study of three-electron correlations. This study shows a peculiar transition, or crossover, of short-range electron correlations, between triangular below half-filling, to honeycomb above half-filling [33, 34];

(ii) The validity of Halperin-type spin-compensated wavefunctions for filling  $5/2$ , denied in the past on the grounds that they do not represent global spin singlets, has been reconfirmed. Spontaneous breaking of spin symmetry is demonstrated, and is shown to be associated with a previously hidden order parameter [35].

### 3.7 New methods and techniques

Among the new methods and techniques developed in the course of this project, two in particular have been considered to be of more general interest, and have been separately published.

(i) We have devised and perfected our own version of fermionic quantum Monte Carlo simulation method. It is based on the Sugiyama-Koonin idea of not integrating out the fermionic degrees of freedom, and propagating instead a Slater determinant in imaginary time. This work, and the ideas it has generated, has had an important role in the quantum Monte Carlo community [36].

(ii) The problem of handling quantum effects inside an otherwise classical simulation, is recurrent and unsolved. We have shown how in principle the problem can be solved by adding a new artificial piece to the hamiltonian, whose role is to force the system to avoid energies which are far from



eigenvalues. The method can be used both for obtaining correct canonical averages, and for energy-conserving propagation of an excited state [34].

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